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SINGLET-OXYGENATION OF A CONJUGATED DIALLENE: ATTEMPT TO PREPAR--ETC(U)

AUG 82 R C MEBANE, G B SCHUSTER

N00014-76-C-0745

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Diallene Singlet oxygen Divinyl peroxide chemiluminescence		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A conjugated diallene, 2,3-divinylidenebicyclo[2.2.1]heptane, was prepared and isolated. Photosensitized oxygenation of this allene leads to two isolated oxygenated products in 50% yield. Detection of these products is interpreted to implicate an unstable cyclic divinyl peroxide intermediate. Attempts to detect this intermediate by low temperature nmr spectroscopy and by chemiluminescence were unsuccessful. The instability of this compound is attributed to the destabilizing lone pair interaction of the peroxide oxygen atoms.		

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Singlet-Oxygenation of a Conjugated Diallene:
Attempt to Prepare a Stable Divinyl Peroxide.

by

Robert C. Mebane and Gary B. Schuster

Prepared for Publication

in

Journal of Organic Chemistry

School of Chemical Sciences

University of Illinois

Urbana, Illinois 61801

August 20, 1982

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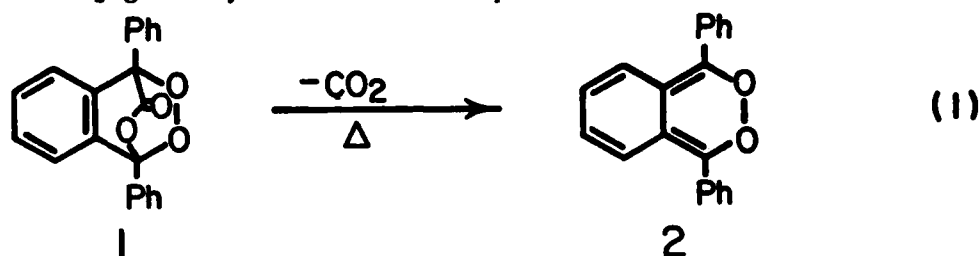
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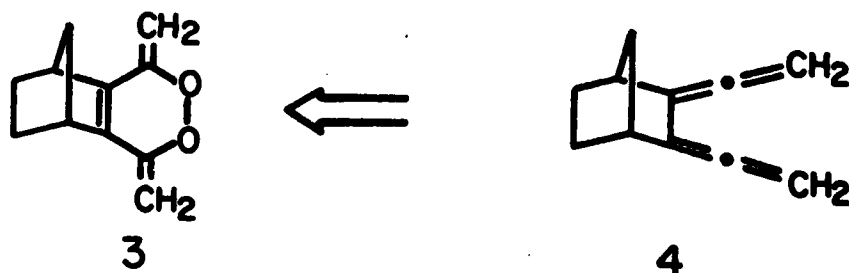


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Recent advances in the thermal chemistry of organic peroxides have provided further insight into the mechanism of electronically excited state generation and into the processes of chemiluminescence.¹ Part of our continuing interests in this field has been concerned with the identification of new chemiluminescent systems through the synthesis and investigation of novel compounds containing this functional group. The discovery² that thermolysis of endoperoxide **1** generates a vinyl peroxide (**2**) with modest thermal stability (eq 1) prompted us to search for other examples of this class of conjugated cyclic unsaturated peroxide.



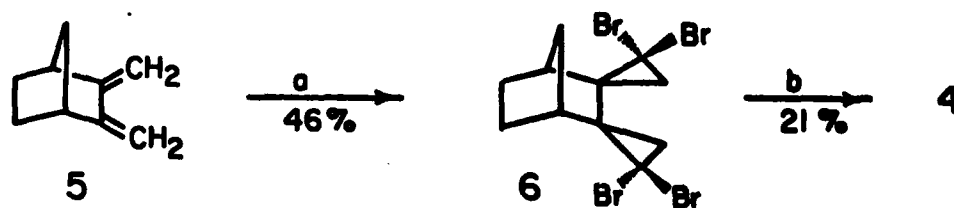
Vinyl peroxides have been implicated as intermediates in several chemical reactions.^{3,4} Examples include the co-oxidation of phenylacetylene and thiols with molecular oxygen³ and the cycloaddition of singlet molecular oxygen to conjugated vinyl allenes.⁴ We chose as our target molecule compound **3** on the assumption that this divinyl peroxide contains geometric constraints that force the oxygen-oxygen σ -bond to be in a plane orthogonal to the molecules π -system, and that this feature might stabilize this inherently reactive peroxide linkage.⁵ This report deals with our attempt to prepare **3** by the cycloaddition of singlet molecular oxygen ($^1\text{O}_2$) to conjugated diallene **4**: the results of which are relevant to the synthesis of conjugated cyclic unsaturated peroxides.



The synthesis of **4** is illustrated in Scheme I. The starting bicyclic diene (**5**) is conveniently prepared by the procedure described by Bowe et al.⁷ The addition of two equivalents of dibromocarbene to this compound to give **6** was done by the two-phase method⁸ of dihalocarbene generation using tri-n-butylamine⁹ as the phase transfer catalyst. The details of the structural assignment of **6** are presented in the Experimental Section. It is interesting to note, however, that the prediction, based on molecular models, that a trans relationship of the dibromocyclopropyl appendages is preferred in **6** is supported by the asymmetry exhibited by the resonances in the ¹H-NMR spectrum, and more notably in the proton-decoupled ¹³C-NMR spectrum of this compound.

Formation of the diallene is accomplished by treatment of a solution of **6** and tetramethylenediamine in ether at reduced temperature with an excess of lithium bromide complexed methyllithium for 0.5 h.¹⁰ Analysis of the initial mixture from this reaction reveals only one product. However, after a suitable extractive workup at room temperature several products are observed. Chromatography of this mixture on neutral alumina (activity V) with pentane followed immediately by flash distillation of the appropriate concentrated fraction at reduced pressure gives the diallenic compound **4** (21%) in greater than 95% purity.¹¹ The difficulties encountered in the purification of **4** are compounded by the fact that this compound decomposes rapidly at room temperature.¹² Thus, all subsequent reactions of **4** were conducted immediately after completion of its purification.

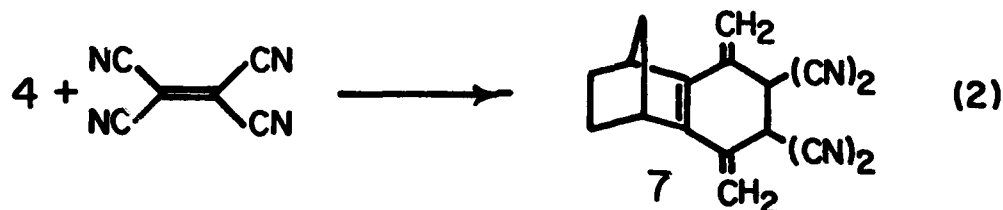
Scheme I



a) CH₃Br, 50% Aqueous NaOH, (n-butyl)₃N, CH₂Cl₂, 50° C, 16 h.

b) LiBr·MeLi, TMEDA, Et₂O, -78° C, 0.5 h.

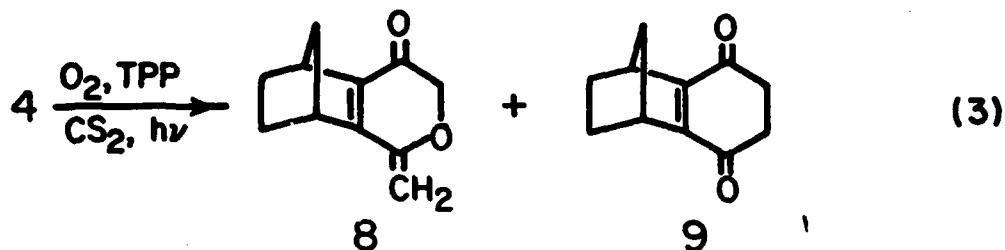
The structure of the isolated diallene was confirmed by spectroscopic and chemical methods. Diagnostic signals in the $^1\text{H-NMR}$ spectrum of **4** are noted at $\delta 4.8$ (4H, s, $=\text{C}=\text{CH}_2$)¹³ and $\delta 2.9$ (2H, broad s, bridgehead protons). The infrared spectrum of this compound clearly exhibits an absorption at 1960 cm^{-1} (asymmetric stretch of the allene) and at 850 cm^{-1} (terminal methylene stretch).¹⁴ Also consistent with the structural assignment of **4** is an ion at $m/e\ 144\ (\text{M}^+)$ in the mass spectrum. Further structural proof of **4** was obtained by characterization of the adduct (**7**) formed with tetracyanoethylene (TCNE), eq 2. An exhaustive attempt was not made to elucidate the structure(s) of the decomposition product generated during the purification of **4**; However, the $^1\text{H-NMR}$ spectrum of this product strongly suggests polymeric material.¹⁵



The decision to incorporate the conjugated diallene function in a bicyclic [2.2.1] ring system proved to be judicious in that not only does it provide rigidity for the carbon framework of the peroxide, but the ability of the diallene system to undergo internal cycloaddition⁶ is apparently diminished. Also, complicating ene reactions during the $^1\text{O}_2$ reaction are eliminated.

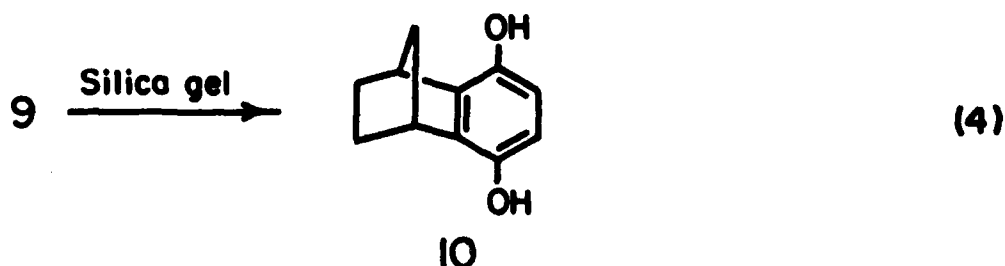
Irradiation ($>400\text{ nm}$) of an oxygen saturated solution of **4** and tetraphenylporphine in carbon disulfide at room temperature leads to rapid consumption of the diallene as determined by $^1\text{H-NMR}$. It is apparent from the spectrum that only two major products are formed during the dye-sensitized photooxygenation (eq 3). Neither product survives conventional chromatographic

techniques. However, they are easily isolated by HPLC (8% isopropanol/hexane) using a Partisil PAC-10 (Whatman) column housed in a glass jacket and cooled to -20°C .



The photooxygenation products from **4** are identified as ketoenol ether **8** (29%) and diketone **9** (21%).¹⁶ In the case of **8**, two broad singlets corresponding to bridgehead protons are observed at $\delta 3.1$ (1H) and 3.25 (1H) in the ^1H -NMR spectrum and suggest an asymmetrical bicyclo [2.2.1] structure. Vinyl proton absorptions consistent with the ^1H -NMR substitution of enol ethers are exhibited at $\delta 4.5$ (1H, s) and 4.65 (1H, s).¹⁷ Further, a doublet centered at $\delta 4.15$ (2H, $J=3$ Hz) is noted in the spectrum and is assigned to the methylene protons α to the carbonyl group and the ether linkage.¹⁸ These ^1H -NMR features along with appearance of a strong carbonyl absorption at 1675 cm^{-1} ¹⁹ in the IR spectrum of **8** form the basis of the structural assignment of this compound.

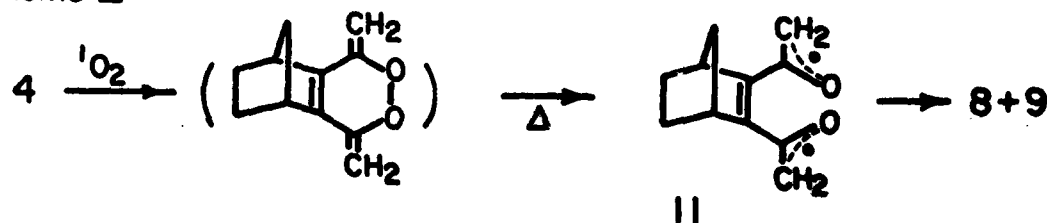
The IR and ^1H -NMR spectra of **9** are totally consistent with the proposed structure (see the Experimental Section for spectral details). Proof for the structure of **9** is obtained by isomerizing it with silica gel to a compound with spectral and chromatographic properties identical with an authentic sample of 3,6-dihydroxybenzonorborane (**10**), eq 4.



To determine the contribution, if any, of a photoinitiated free-radical process²⁰ to the formation of the observed products from **4**, the photolysis in the presence of a radical initiator was investigated. Thus irradiation (350 nm) of an oxygen saturated carbon disulfide solution of **4** and tert-butyl peroxybenzoate (10 mol %) results in complete consumption of **4** after 45 min. Neither of the two products, **8** or **9**, are detected in the sample by ¹H-NMR spectroscopy. This result is consistent with the finding that the yield of **8** and **9** are not affected by inclusion of 3,6-di-tert-butyl-4-methylphenol (BHT), a free radical inhibitor, in the dye-sensitized photooxygenation of **4**. These findings indicate that the disappearance of **4** during the photooxygenation is a result of its reaction with singlet molecular oxygen. Further evidence for this conclusion comes from the observation that diallene **4** quenches the infrared emission of ¹O₂ in CS₂ solution with a bimolecular rate constant of $3.3 \times 10^6 \pm 1.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

The reactions of ¹O₂ with conjugated diene systems have been extensively studied and usually give cyclic peroxides.²¹ Mechanistically this reaction proceeds by a [4+2] cycloaddition pathway. In the present study a similar reaction is proposed, and as seen in Scheme II, is consistent with the formation of **8** and **9**. Thus, cycloaddition of ¹O₂ to **4** forms the divinyl peroxide **3** which homolytically cleaves under the reaction conditions to diradical **11**. Intramolecular combination of the radicals logically gives the observed products.

Scheme II



In an attempt to gather evidence for the existence of $\mathfrak{3}$ the dye sensitized photooxygenation of $\mathfrak{4}$ was performed at low temperature (-78°C) and the resulting sample was analyzed by ^1H -NMR with the probe temperature maintained at -60°C .²³ The only resonances observed in the spectrum under these conditions are those previously assigned to $\mathfrak{8}$ and $\mathfrak{9}$. Similarly, no chemiluminescence, above a very low background level, can be detected when a solution of $\mathfrak{4}$ photooxygenated at -78°C is warmed to room temperature. Thus, it appears that $\mathfrak{3}$, if it is indeed formed in the oxygenation reaction, does not enjoy the thermal stability hoped for.

Conclusion

This investigation has revealed that the diallene $\mathfrak{4}$ reacts rapidly with singlet molecular oxygen - a result which may be general and of synthetic utility. The two products isolated from this reaction are found to have incorporated two oxygen atoms. Although a precursor to these products is not detected, it seems reasonable to assume, after considering the reaction of $^1\text{O}_2$ with conjugated diene systems, that a short-lived intermediate does exist and is probably the anticipated divinylperoxide $\mathfrak{3}$. The apparent instability of this peroxide is puzzling in comparison to related diacyl peroxides such as phthaloyl peroxide. A reasonable cause for this difference is that the very strong four-electron repulsive interaction of the oxygen lone pairs in these enforced planar structures is relieved by delocalization into the electron withdrawing carbonyl groups of the diacyl peroxide and cannot be so accommodated by the methylene groups of the vinyl peroxide.

Experimental Section

General. Proton magnetic resonance spectra were recorded on a Varian EM-390 spectrometer. A JEOL JNM-FX 60 FT-NMR was used to obtain ^{13}C -NMR spectra. Chemical shifts are relative to tetramethylsilane. IR spectra were recorded on either a Perkin Elmer 237B grating infrared spectrophotometer or a Nicolet 7199 FT-IR instrument. High-performance liquid chromatography (HPLC) was performed on a Perkin-Elmer Series 2 chromatograph equipped with a Perkin-Elmer LC-75 variable wavelength detector. Mass spectra were obtained with a Varian MAT CH-5 mass spectrometer. Elemental analyses were performed by J. Nemeth and Associates, Dept. of Chemistry, University of Illinois, Urbana, Illinois. Melting points were determined on a Büchi apparatus by the capillary method and are uncorrected.

Materials

All reaction solvents were either spectroscopy grade or were purified by standard techniques. The hexane (Burdick and Jackson distilled in glass) used in preparative HPLC was purified by washing successively with concentrated sulfuric acid, water, and a saturated aqueous solution of sodium carbonate. It was then dried (calcium chloride), passed through a basic alumina column (activity I) and then distilled.

2,3-Dimethylenebicyclo[2.2.1]heptane (5) was prepared by the method of Bowe *et al.*⁷ except that diimide²² was used to reduce 5,6-dichloromethylbicyclo[2.2.1]-hept-2-ene.

d,ℓ-Dispiro[bicyclo[2.2.1]heptane-2,1'-2,2'2'-dibromocyclopropane-3,1"-2",2"-dibromocyclopropane] (6). A two phases mixture consisting of diene (5) (5.0g, 4.2×10^{-2} mol), methylene chloride (100 mL), bromoform (84.6g, 0.334 mol), 50% aqueous sodium hydroxide (150 mL) and tri-*n*-butylamine (100 mL) was vigorously stirred by a mechanical stirrer for 16 hr at 50° under a nitrogen atmosphere.

The crude reaction mixture was diluted with methylene chloride (200 mL) and this organic solution was washed successively with water (3 x 100 mL), 10% aqueous hydrochloric acid (3 x 100 mL) and water (2 x 100 mL). The organic layer was dried (MgSO_4) and the solvent removed by rotary evaporation. The dark brown crude material obtained was flushed through silica gel with hexane. This hexane solution was concentrated by rotary evaporation and the residue was subjected to vacuum distillation to remove the excess bromoform. The pot residue was cooled to -20°C whereupon the viscous oil solidified. This crude crystalline material was recrystallized from ethanol/pentane to afford 9.1 g (46%) of white crystals: mp $117-118^\circ\text{C}$, H-NMR (CDCl_3) δ 1.0 - 2.1 (8H,m), 2.2 (1H, broad s), 2.7 (1H, broad s), 3.1-3.7 (2H, AB, $\delta_A = 3.12$, $\delta_B = 3.61$, $J_{AB} = 9$ Hz); ^{13}C -NMR (CDCl_3) δ 25.8, 26.1, 27.5, 28.6, 34.1, 36.5, 37.7, 41.4, 41.7, 53.2, 54.05. Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{Br}_4$: C, 28.48; H, 2.61; Br, 68.91. Found: C, 28.67; H, 2.45; Br, 69.06.

2,3-Divinylidenebicyclo[2.2.1]heptane (4). To a magnetically stirred diethyl ether solution (15 mL) of the tetrabromide (6) (0.50g, 1.08×10^{-3} mol) and tetramethylethylenediamine (10 μL) under a nitrogen atmosphere and cooled to -78°C was added dropwise a diethyl ether solution of lithium bromide complexed methyl lithium (8.6 mL, 4.32×10^{-3} mol). The reaction was stirred at -78°C for 30 min and then methanol (0.5 mL) was added and the resulting solution was warmed to room temperature, diluted with ether (100 mL), extracted with ice water (3 x 30 mL) and dried (K_2CO_3). The solvent was removed by rotary evaporation and the residue was passed quickly through an alumina column (neutral, activity V, 15g) using pentane as the elutant. The yellowish oil obtained after removal of the solvent (0.10g, 64%) was found by ^1H -NMR to be mostly the desired diallene 4. Purification was accomplished by flash distillation at room temperature under reduced pressure ($< 10^{-4}$ torr) using a sublimation apparatus in which the cold finger was cooled to liquid nitrogen temperature. The colorless oil (32×10^{-3} g, 21%) has the following spectral characteristics: ^1H -NMR (CCl_4) δ 1.0-2.0 (8H,m),

2.9 (2H, broad s), 4.8 (4H, s); IR (Film) cm^{-1} 1960(m), 850(m); MS (70 ev) m/e (relative intensity) 144 (m^+ , 37), 128 (33), 117 (41), 116 (37), 115 (100), 91 (36).

TCNE Adduct of Compound (4). A carbon tetrachloride solution (5 mL) of 4 (3.4×10^{-2} g, 2.36×10^{-4} mol) and tetracyanoethylene (2.7×10^{-2} g, 2.1×10^{-4} mol) was stirred at room temperature under nitrogen for 6 h. The solvent was removed by rotary evaporation and the residue was purified by preparative HPLC (3% isopropanol/hexane, Perkin-Elmer Silica A, 10 μ particle size, 9 mm x 25 cm) to afford adduct (7), (21.2×10^{-3} g, 37%) which has the following spectral properties: $^1\text{H-NMR}$ (CCl_4) δ 1.0-2.0 (6H, m), 3.2 (2H, broad s), 5.7-5.9 (4H, AB, $\delta_A = 5.7$, $\delta_B = 6.1$, $J_{AB} = 3$ Hz). Exact mass calcd for $\text{C}_{17}\text{H}_{12}\text{N}_4$ m/e 272.1062, found m/e 272.1064.

General Procedure for the Dye Sensitized Photooxygenation of 4. A solution of 4 (24×10^{-3} g, 1.66×10^{-4} mol) and tetraphenylporphyrin (2×10^{-3} g) in carbon disulfide (30 mL) was saturated with oxygen and then maintained under an oxygen atmosphere while being irradiated with the output of a 250 W Tungsten-Halogen lamp filtered through a Corning CS3-73 glass plate (> 400 nm) for 4 min at room temperature. The solvent was removed to give the crude product. Product yields were obtained by dissolving the crude product and chloroform (internal standard) in carbon disulfide (1 mL) and integrating the appropriate peaks in the $^1\text{H-NMR}$ spectrum (9, 21%; 8, 29%). Compounds 8 and 9 were separated by HPLC on a Whatman Partisil PAC-10 column (9mm I.D. x 50 cm) using 8% isopropanol/hexane as the elutant. The column was housed in a glass jacket and was cooled to -20°C by means of a recirculating bath. The products were monitored at 270nm by uv (8, $V_R = 37$ mL; 9, $V_R = 72$ mL).

Compound 8 has the following spectral properties: $^1\text{H-NMR}$ (CS_2) δ 1.0-2.0 (7H, m), 3.1 (1H, broad s), 3.25 (1H, broad s), 4.15 (2H, d, $J = 3\text{Hz}$), 4.5 (1H, s), 4.65 (1H, s); IR (CS_2) cm^{-1} 2964 (m), 2866 (m), 1675 (s), 1102 (m).

Compound 9 has the following spectral characteristics: $^1\text{H-NMR}$ (CS_2) δ 1.0-2.0 (6H, m), 2.7 (4H, m), 3.35 (2H, broad s); IR (CS_2) cm^{-1} 2964 (m), 2873 (m), 1676 (s). A sample of this material was stirred at room temperature with silica-gel (1 g) in diethyl ether (5 mL) for 5 min. Filtration of the solution followed by removal of the solvent by rotary evaporation afforded a compound with spectral properties identical to an authentic sample of 3,6-dihydroxybenzonorborane (10) (Chemalog). A homogenous peak ($V_R = 16$ mL) was noted when a sample of 9 and the rearranged product were co-injected during an HPLC analysis (Perkin-Elmer Silica A, 10 μ , 2.6 mm I.D. x 25 cm; 3% isopropanol/hexane).

Photolysis of 4 and tert-Butyl Peroxybenzoate. Under an oxygen atmosphere a solution of 4 (21×10^{-3} g, 1.46×10^{-4} mol) and tert-butyl peroxybenzoate (3 mg, 10 mol %) in carbon disulfide (1 mL) was irradiated in a Rayonet (350 nm) until it was determined by $^1\text{H-NMR}$ that all of the diallene was consumed (75 min). No resonances were observed in the region between δ 3.0-5.0 (complex multiplet seen in methylene region) in the $^1\text{H-NMR}$ spectrum of the reaction product.

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